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Synthesis of ultrafine spherical YAG:Eu^{3+} phosphors by MOCVD

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ABSTRACT

Ultrafine Europium-doped yttrium aluminum garnet (YAG:Eu^{3+}) phosphor powders, with uniform diameters of about 1 μm, have been prepared by metallorganic chemical vapor deposition (MOCVD). The metal–organic precursors have been characterized by thermogravimetry–differential scanning calorimeter (TG–DSC). The phosphor powders have been identified by X-ray diffraction (XRD), scanning electron microscope (SEM) and photoluminescence measurements. It shows that the YAG:Eu^{3+} particles annealed at 1473 K for 3 h are nonaggregated and spherical, the diameter of particles is in the range of 1–2 μm. Phase-pure YAG which is of spherical shaped particles have been obtained and observed good luminescence property. Three major emission peaks were observed at 589, 594, and 607 nm.

1. Introduction

The development in the field of high resolution and efficiency displays has an urgent need for phosphors with novel and enhanced particle properties [1,2]. In the design of powder phosphors, the ideal morphology is that of a perfect sphere [3]. Spherical morphology phosphors, with uniform diameters of about 1 μm, can bring high brightness and high resolution of display [4]. The advantages of the host crystal with $Y_3Al_5O_{12}$ (abbreviated as YAG) are relatively stable lattice and large heat conductivity, so YAG can be used as the host lattice for a number of phosphors [5]. Conventionally, the YAG based phosphors have been commonly prepared by solid-state reaction running for several hours at high temperature such as nearly 1873 K, and prolonged heating process can avoid the formation of the phases of $YAlO_3$ (YAP) and $Y_4Al_2O_9$ (YAM) [6–8]. But crystal will grow because of high temperature and long heating time.

In the past few years, various improved methods, such as sol–gel [9,10], combustion [11], spray pyrolysis [12,13] have been utilized to synthesize ultrafine YAG phosphor. However, it is difficult to control the morphology of phosphors by these methods. In recent years, there are growing attentions on MOCVD for metallic oxides preparation [14,15], due to its simple operation and versatile precursors. Here we report the MOCVD synthesis, luminescence properties of YAG:Eu^{3+} phosphors.

2. Experimental section

Fig. 1 shows the CVD system for YAG:Eu^{3+} phosphor powders preparation, which consists of vapor generators and a high temperature deposition reactor. Aluminum nitrate ($Al(NO_3)_3$ $9H_2O$, analytical grade), Yttrium nitrate ($Y(NO_3)_3$ $6H_2O$, analytical grade), Europium nitrate($Eu(NO_3)_3$ $9H_2O$, analytical grade) and 2,2,6,6-tetramethylheptane-3,5-dione (HDPM, analytical grade) were used as starting materials in the present synthesis. HDPM served as chelating agent to metal cation and fuel for combustion. All precursors including Y(DPM)3, Eu(DPM)3, and Al(DPM)3 remained by sol–gel were respectively recrystallized from cyclohexane.

As shown in Fig. 1, $Y(DPM)_3$, $Al(DPM)_3$ and $Eu(DPM)_3$ were vaporized and then carried with nitrogen gas separately. After mixing with oxygen, the vapor was led in a tubular reactor. The vaporizing temperatures of $Y(DPM)_3$, $Eu(DPM)_3$ and $Al(DPM)_3$ were regulated separately according to the results of thermal analysis, which can ensure the full evaporization of precursors without any decomposition in the evaporization zone. The ratio of Y:Eu:Al in the formula of $Y_{3-x}Eu_xAl_5O_{12}$ could be controlled by changing nitrogen gas flow rate and evaporation temperatures. The vaporizing temperatures of $Y(DPM)_3$, $Eu(DPM)_3$ and $Al(DPM)_3$ were 493–543 K, 513–563 K and 463–513 K respectively, the depositing temperature was 923–973 K, the gas flow rate (Nitrogen carrier) of Oxygen, $Y(DPM)_3$, $Eu(DPM)_3$ and $Al(DPM)_3$ were separately 150 ml/min,75–100 ml/min, 4–6 ml/min and 75–100 ml/min.

The thermogravimetry–differential scanning calorimeter (TG–DSC) (Germany, NETZSCH STA449 C) measurements were performed at a heating rate of 10 K/min in air to determine the volatility and decomposition temperature of the precursors. X-ray measurements were done for verification of crystallinity and formation of YAG:Eu^{3+}. The particle size and morphology was examined using scanning

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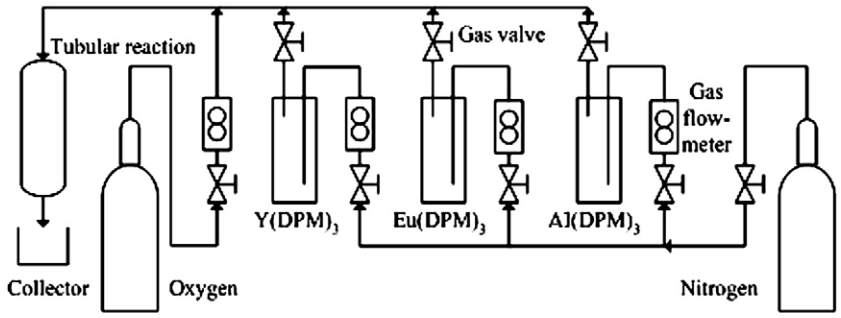

Fig. 1. Schematic and experimental conditions of MOCVD apparatus for generation of YAG powders.

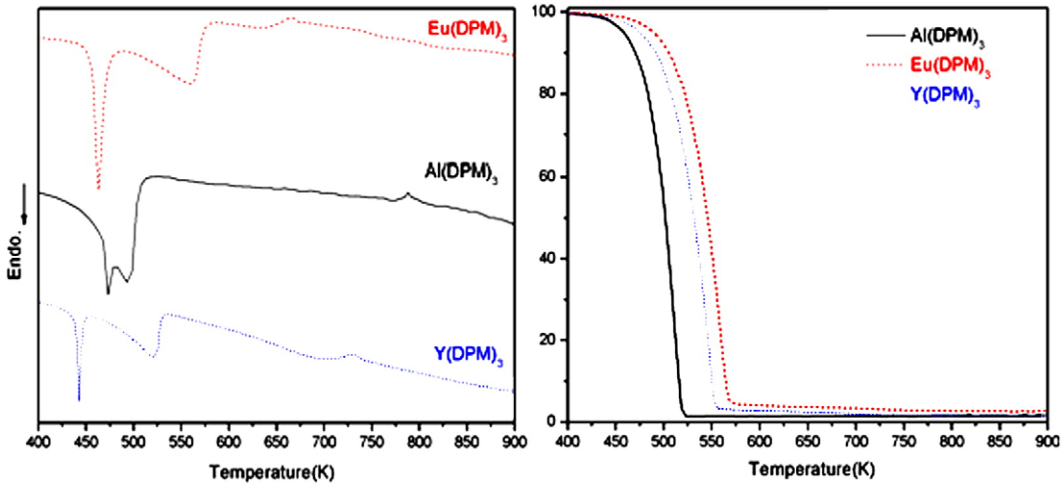

Fig. 2. TG–DSC curves for $Y(DPM)_3$, $Al(DPM)_3$ and $Eu(DPM)_3$.

electron microscope images (SEM) (Germany, LEO-1530). The photoluminescence of the synthesized YAG:Eu^{3+} was taken by a fluorescence spectrometer (Hitachi, F-4500) at room temperature.

3. Results and discussion

3.1. Thermal analysis of precursors

Fig. 2 shows the TG–DSC results of the precursors $Y(DPM)_3$, $Al(DPM)_3$ and $Eu(DPM)_3$ in nitrogen gas. The mass of $Al(DPM)_3$, $Y(DPM)_3$ and $Eu(DPM)_3$ decreased rapidly at around 443 K, 443 K and 473 K due to their evaporation, and no further mass loss was observed when the temperature exceeded 523 K, 553 k and 573 K for each precursor. In the DSC curves, the decomposition and oxidation behavior were associated with a very large exothermic peak for the every sample by oxygen at the temperature of 703–753 K for $Y(DPM)_3$, 763–813 K for $Al(DPM)_3$ and 633–683 K for $Eu(DPM)_3$ respectively. The differences of volatile temperatures among $Y(DPM)_3$, $Al(DPM)_3$ and $Eu(DPM)_3$ were suggestive of the volatile temperature directly in proportion to the molecular mass. In order to fully evaporate all precursors, the temperatures were regulated within the ranges of 463–513 K, 493–543 K, and 513–563 K for $Y(DPM)_3$, $Al(DPM)_3$ and $Eu(DPM)_3$, respectively.

3.2. XRD identification

Fig. 3 shows the XRD pattern of the YAG:Eu^{3+} phosphors prepared from MOCVD process. The identical diffraction pattern of YAG:Eu^{3+} is suggestive of phase-pure crystalline [16]. A theoretical one for comparison, which shows the partial substitution of rare earth ion Eu^{3+} by Y^{3+} did not affect the cubic structure, but a clearly seen small shift of the observed peak positions to the lower angles is expected as Eu^{3+} ions must necessarily expend the original YAG cubic cell since it is noticeably larger than the substituted Y^{3+} ion.

3.3. Morphology, microstructure

The SEM images of YAG:Eu^{3+} phosphors prepared by solid-state reaction and MOCVD were shown in Fig. 4. It is obvious that most of the particles prepared by MOCVD are almost spherical, the diameter of particles is in the range of 1–2 μm, no agglomeration was observed. The YAG:Eu^{3+} phosphors particles prepared by solid-state reaction were severely damaged. A majority of the particles agglomerated together and did not have regular spherical shape, because the extreme milling was necessary to decrease the agglomeration.

3.4. Luminescence properties

Photoluminescence properties of YAG:Eu^{3+} was studied at room temperature under the excitation of 236 nm UV–VIS light. Fig. 5 depicts the excitation and emission spectra

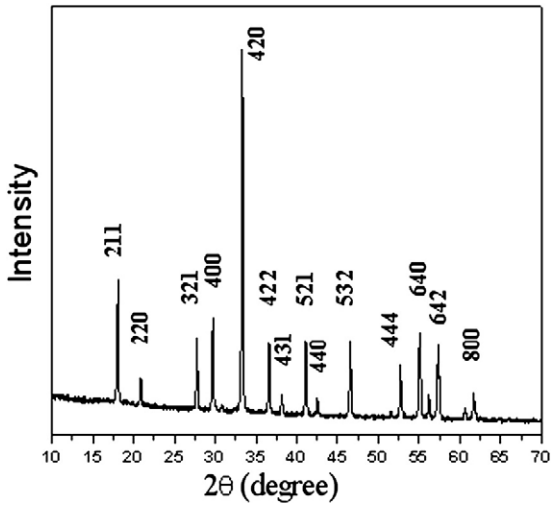

Fig. 3. XRD patterns of YAG powders derived from MOCVD method. Experimental conditions: as-prepared temperature, 923–973 K; annealing temperature, 1473 K (3 h).

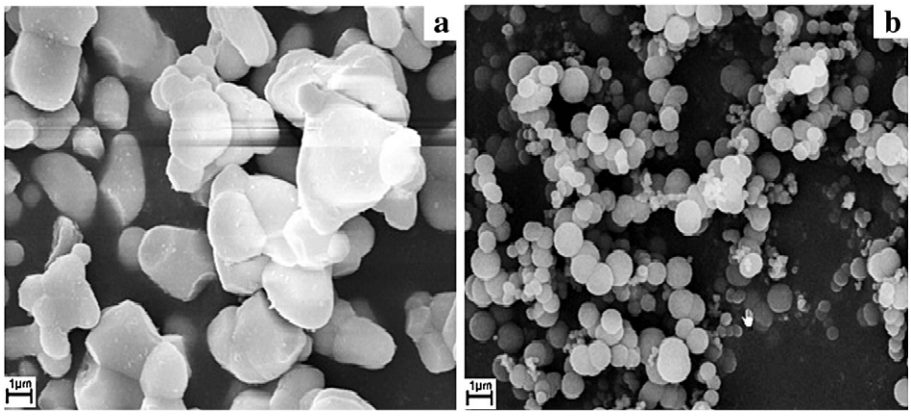

Fig. 4. SEM images of YAG:Eu^{3+} phosphors derived from (a) the solid-state reaction at 1823 K for 4 h and (b) the MOCVD method at 1473 K for 3 h.

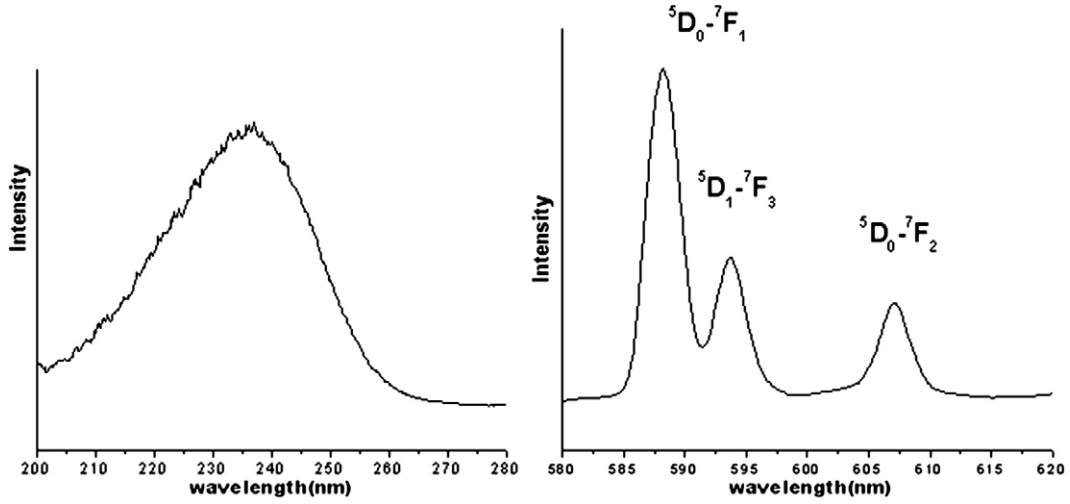

Fig. 5. Excitation and Emission spectrum of MOCVD derived YAG:Eu^{3+} phosphors. Experimental conditions: as-prepared temperature, 923–973 K; annealing temperature, 1473 K (3 h).

of YAG:Eu^{3+} phosphors. Three major emission peaks were observed at 589, 594, and 607 nm, revealing the characteristic emission properties of the Eu^{3+} activators. The greatest emission at 589 nm occurred from $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+}. The $^5D_1 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_2$ transition processes of Eu^{3+} were responsible for the emission at 594 and 607 nm, respectively [16–18].

4. Conclusions

In summary, the approximate uniform diameter YAG:Eu^{3+} phosphor powders have been successfully synthesized by the MOCVD method. The thermogravimetry–differential scanning calorimeter (TG–DSC) analysis found that the reasonable deposition temperature was in the range of 923–973 K. The SEM images showed that micro-size YAG:Eu^{3+} phosphor particles were spherical morphology and evenly dispersed. The YAG:Eu^{3+} particles had good photoluminescence characteristics. The approach in this paper is a feasible method to fabricate YAG:Eu^{3+} phosphor particles.

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